Growth, synthesis and characterization of divalent cations doped single crystals

Synopsis submitted to the Mangalore University for the partial fulfillment of

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by

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Process of phase transformation alters inherent physical and electro-chemical properties of a substance under test. The behavioral changes explicitly demonstrated in liquefaction of gases, nano-fabrications, superconductors, etc [1]. Apparently, according to laws of symmetries of nature, one could expect similar behavioral changes during crystallization of substance when subjected to phase transformation. Henceforth, a pronounced work has been conducted on the growth of metallic, insulator (ceramics) and semiconductor crystals [2, 3]. Cationic doping in crystals produced multiple structural geometries, which possessed distinct physical, chemical, opto-electro-magnetic and dielectric properties. As an impact of phase transformation, by selective doping and co-doping a variety of crystalline materials were grown which find spectrum of applications [4, 5].

Many crystallographers published their investigation on fabrication of silica gel treated doped phosphate and oxalate crystals using gel technique; betrayed the physico-chemical properties and applications. As per the literature, oxalate and phosphate crystals grown using gel method are water insoluble, pure and defect free, exhibit corrosion resistance, good mechanical and dielectric strength, insulating/semiconducting properties, few ingrained piezo and ferro electric properties, excellent leakage resistance (GΩ) and capacitance (pF) [6-8].

Moreover, due to flexibility and adaptability of oxalate $(C_2O_4)^{2-}$ and phosphate $(PO_4)^{3-}$ ions enormous doped, co-doped and mixed crystals were grown. Both oxalate and phosphate ions multiplexed with alkaline, rare-earth and transition metal ions produced desperate structural art work in one, two and three dimensional network. In the crystal framework water molecules adjoin with metal ions either as debris or co-ordinated or combination of the two and display spectacular grid pattern [9-11].

Aims and objectives

The research work entitled "Growth, synthesis and characterization of divalent cations doped single crystals'' was carried out at the Post graduate department of Physics, Field Marshal K M Cariappa college (A constituent college of Mangalore University), Madikeri. The investigation comprises of synthesizing *three series* of crystalline materials from phosphoric acid impregnated silica (PIS) and oxalic acid impregnated silica (OIS) gels using gel technique. The crystals were grouped as doped phosphates, co-doped phosphates and doped oxalates. We developed *gel temperature* (G_T) diagram to optimize phosphoric acid and oxalic acid reinforced silica gels; which yielded high quality doped crystals. Further, *crystal growth* (C_G) diagram was explored to demonstrate the growth dynamics of synthesized crystals. The crystals were characterized using spectroscopic and analytic techniques which traverse the physical, chemical and opto-electro-magnetic properties.

- Energy dispersive X-ray spectroscopic (EDAX) analysis to determine the chemical constituents and cationic distribution of foregrounded crystals.
- Fourier transform infrared (FTIR) spectral measurements to identify the functional units.
- Thermo gravimetric studies to unveil decomposition behavior and thermal stabilities.
- Powder X-ray diffraction (PXRD) studies to know crystal geometry and cell parameters.
- Optical properties and band gap energy using UV-visible spectroscopic studies.
- Electrical conductivity measurements, volt-ampere characteristics, dielectric and magnetic properties in succession.
- Impedance and resonance studies.

Organization of the thesis

The thesis entitled "Growth, synthesis and characterization of divalent cations doped single crystals" comprises of six chapters**.**

Chapter 1: Introduction

This chapter gives prominence to importance and applications of doped phosphate and oxalate crystals in industries and laboratories. The chapter emphasizes on scope and objectives of the investigation, describes various crystal growth methods, their classifications and uses. Use of gel technique, types of gels, classification of gel technique, various crystals grown in gel and investigation perpetrated by the gel crystal growers were discussed. It also betrayed the gelling mechanism, structure and role of silica hydro gel in the growth of doped phosphate and oxalate crystals.

Chapter 2: Materials and methods

This chapter unveils the growth methods and characterization techniques employed to examine the intrinsic properties of crystals. It describes the principle and working of instruments used: energy dispersive X-ray analysis (EDAX), scanning electron microscope (SEM), Fourier transform infrared spectroscopic analysis (FTIR), thermo gravimetric analysis (TGA), Powder X-ray diffraction (PXRD), UV-visible spectrophotometer, electrical conductivity meter, Keithley source measuring unit (K-SMU), dielectric constant measuring unit and Gouy balance.

Chapter 3: Growth of divalent cations doped phosphate and oxalate crystals

Chapter 3 betrays in detail: gel optimizing parameters, role of gel temperature, doping and selective co-doping in the search for new crystals and growth dynamics of doped crystals. We have developed G_T *diagram* for optimization of phosphoric acid impregnated silica (PIS) and oxalic acid impregnated silica (OIS) gels and identified NLDJ crystallization zones for each;

which brought all the gel optimizing key factors: specific gravity of sodium meta silicate (SMS), pH of gelling solution, gel density and gel temperature together. G_T diagram aided crystal growth unveiled inherent properties of PIS and OIS gels which yielded high quality doped phosphate and oxalate crystals.

Adopting divalent Ba^{2+}, Zn^{2+} and Sr^{2+} as parent cations, with proper divalent doping cations (Mn^{2+}, Cd^{2+}, Sr^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+} and Ba^{2+}) and selective co-doping cations (Cd^{2+}-Ni^{2+}, Cd^{2+}-Co^{2+} and Co^{2+}-Mn^{2+}) we synthesized *three distinct series* of divalent doped phosphate and oxalate crystals: doped phosphates [eight crystals – calcium doped zinc phosphate (CADZP), manganese doped barium phosphate (MDBP), manganese doped zinc phosphate (MDZP), cadmium doped zinc phosphate (CDZP), barium doped zinc phosphate (BDZP), cobalt doped zinc phosphate (CODZP), nickel doped zinc phosphate (NDZP) and strontium doped zinc phosphate (SDZP)], co-doped phosphates [three crystals– cobalt–manganese co-doped zinc phosphate ((Co-Mn)DZP), cadmium–nickel co-doped zinc phosphate ((Cd-Ni)DZP), and cadmium–cobalt co-doped zinc hydrogen phosphate ((Cd-Co)DZHP)] and doped oxalates [five crystals– manganese doped zinc oxalate (MDZO), cadmium doped zinc oxalate (CDZO), manganese doped barium oxalate (MDBO), strontium doped zinc oxalate (SDZO) and calcium doped strontium oxalate (CADSO)].

The chapter spotlights: faster gel set time of PIS gels than OIS gels, *NLDJ crystallization zone*, optimized gel temperature of 26^{o}C, constancy of gel density factor, ceiling temperature, exponential decay of gel set time with gel temperature for each series of PIS and OIS gels. Growth dynamics of doped phosphate and oxalate were demonstrated using *crystal growth (C_G) diagram* which betrayed: crystal size maximum Cs_o, net growth time t_o, knee time t_k, each stages of growth progress, retardation of growth rate and distinct *NLDJ negative growth rate decay factors* (GR_{DF}) propounded by the crystals. All the doped crystals exhibited exponential growth according to the relation $Cs=Cs_0\ [1- e^{-t/nk}]$ with n=5 for phosphate and n=3 for oxalate crystals. Over all, this chapter provides concrete approach in describing gel optimization and growth kinetics of three series of new doped phosphate and oxalate crystals.

Figure 1. Divalent cations doped phosphate and oxalate crystals.

Chapter 4: Characterization of doped phosphate and oxalate crystals

Chapter 4 gives in-depth characterization of sixteen doped phosphate and oxalate crystals. The foregrounded crystals were characterized by spectroscopic and analytical techniques; their electro-magnetic-dielectric properties were betrayed. EDAX measurement using CARL ZEISS FESEM attached with EDS system (Oxford instruments) explored underlying chemical constituents, cationic distribution, extent of doping and betrayed surface fineness of crystals. FTIR studies with the aid of Fourier transform infrared spectrophotometer (Bruker) in the wave number range 400- 4500cm^{-1} identified functional groups and debris which form basis of developed crystals. TG measurements using

SDT-Q600 (TA instruments) explored degradation behavior and thermal stabilities of the crystals. Combined venture of EDAX, FTIR and TG analysis measured molecular formula and molecular weights of fabricated crystals. Minflex 600 Rigaku diffractometer (X-ray Cu-Kα wavelength 1.54Å) at a scan speed of 1˚/minute was used to study the X-ray diffraction patterns. Using powderX software Bragg's diffraction pattern were indexed and additional refinement was performed adopting chekcell operation.

Impact of UV-visible light on crystals were analyzed with the aid of UV-visible spectrophotometer (UV-1800 SHIMADZU) in the spectral range 190-1200nm. Electrical conductivity measurements of the crystals were recorded using Roy instruments (IR-503, CDM-17076) operated at the conductivity range 0-1000mMho/cm. Dielectric studies were performed using 2151/T-7C (Mittal instruments) calibrated to attain sine wave of frequency 253.88kHz. Keithley source measuring unit (KSU-2450) was used to explore electrical properties. Magnetic susceptibility of individual crystals was determined by Gouy's method (Holmarc: HO-ED-EM-08).

The results of characterization are discussed in brief. EDAX measurements unveiled little uniqueness and some distinctness in doping ratio of crystals. Among doped phosphate crystals, CADZP crystal inborn with a cationic distribution Zn^{2+}:Ca^{2+}=499:1 (*thin doping*); MDZP crystal ingrained with cationic distribution Zn^{2+}:Mn^{2+}=2.6:1 (*heavy doping)*. All the five doped oxalate crystals (CDZO, MDBO, CADZO, SDZO and MDZO) showed uniqueness in cationic distribution with doping ratio less than 5:1, hence become heavily doped and behave as *mixed crystals*. EDAX measurements also rectified co-doping in (Co-Mn)DZP, (Cd-Ni)DZP and (Cd-Co)DZHP crystals with distinct cationic distribution Zn^{2+}:Mn^{2+}:Co^{2+}=33.09:5.591:1, Zn^{2+}:Ni^{2+}:Cd^{2+}=21.891:2.425:1 and Zn^{2+}:Co^{2+}:Cd^{2+}=260.5:16.277:1 respectively. EDAX results reveal selective doping is one of the important tool in the fabrication of new (crystalline) materials. Crystals such as CADZP and CADSO resembled kidney stones; due to their biological importance the growth parameters and characterization results were demonstrated in comparison with clinically collected renal stones. FTIR spectra showed the presence of OH group, C-C, C=O, C-O and M-O (M-metal cation) bonds in doped oxalate crystals. Distinctly, among doped and co-doped

phosphate crystals P=O, P-O, P-OH, M-O bonds form the crystal armature. TG studies explicitly betrayed inherent thermal properties, decomposition phases, thermal stability and existence of coordinated and crystalline water in the crystals. Except MDBP crystal, all the doped phosphate crystals ingrained with co-ordinated and crystalline water, exhibited thermal stability up to 800^{o}C in M_3-$(PO_4)_2$ state; MDBP possesses only crystalline water and remain thermally stable upto 600^{o}C in Ba:Mn-O (oxide state). CODZP, NDZP, MDZP, BDZP and MDBP exhibited only two decomposition phases until the temperature of 500^{o}C, where as CDZP, CADZP and SDZP crystals exposed three degradation phases until 800^{o}C. All the doped oxalate crystals except MDBO and CADSO exhibited thermal stability above 550^{o}C in metal oxide state. Surprisingly, MDZO exhibited decomposition in four stages till the temperature of 600^{o}C and possesses both coordinated and crystalline water. MDBO involves three phases of decompositions until 550^{o}C and remain stable in Ba:Mn-CO_3 (carbonate) state. Further, CDZO, CADSO and SDZO showed only two structural deformations and indulge only one crystalline water molecule each. Interestingly, selective co-doping modified decomposition behaviors of co-doped crystals. (Co-Mn)DZP crystal was a constitution of four crystalline waters, one coordinated water, exhibited only two decomposition phases and thermal stability upto 600^{o}C. (Cd-Ni)DZP crystal consists of three crystalline and one coordinated water molecule, showed only two phases of deformation and possessed thermal stability upto 500^{o}C in $(Zn:Cd:Ni)_3$-$(PO_4)_2$ state. Distinctly, (Cd-Co)DZHP ingrained with only one crystalline water, unveiled two deformations with thermal stability upto 500^{o}C in pyrophosphate state. All the sixteen doped crystals were born with distinct molecular weights. MDBP produced as heaviest molecule with a molecular weight of 630.714 and co-doped (Cd-Co)DZHP crystal became the lightest born with a molecular weight of 179.164.

PXRD studies reveal high crystallinity of doped phosphate and oxalate crystals. Among doped oxalates, CDZO, MDBO and SDZO possess monoclinic geometry, CADSO exists in tetragonal and MDZO in orthorhombic system. Except BDZP (monoclinic), all the doped phosphate crystals (CODZP, NDZP, CDZP, MDZP, CADZP, MDBP and SDZP) uniquely joined to orthorhombic system.

Further, co-doped (Co-Mn)DZP and (Cd-Ni)DZP crystals belong to orthorhombic system, whereas (Cd-Co)DZHP come out with monoclinic geometry.

Doped phosphate and oxalate crystals were found transparent to visible light and showed absorption maxima in UV region. UV-visible spectrum with the aid of tauc plot was used to measure the band gap energies. (Cd-Co)DZHP possessed comparatively smallest band gap energy (5.75eV) with a low leakage resistance (R_L=1.211GΩ); while SDZO exhibited large band gap energy (E_g=6.26eV) and very high leakage resistance (R_L=22.346GΩ). Dielectric studies unveiled high dielectric constant ϵ_r =112.51 for (Co-Mn)DZP crystal with crystal capacitance 195.99pF and minimum for MDZO crystal showing ϵ_r =12.51 and low crystal capacitance 21.775pF.

All the doped crystals showed linear growth of electrical conductivity with temperature. Temperature coefficient of electrical conductivity σ_k varies from 0.095S/m/^{o}C (SDZO crystal) to 0.613S/m/^{o}C (CDZO crystal) and distinct for each of the doped crystal. Volt-ampere characteristics of grown crystals exhibited linear growth profile and all the crystals permitted extremely low current (nA) to flow through them. The crystals showed feeble magnetism with molar susceptibility χ; ranges from -2.13× 10^{-4} to 12.16× 10^{-6}cm^3/mol. The crystals such as CADSO, CDZO, SDZO, CADZP, CDZP, BDZP and SDZP exhibited *diamagnetism*; whereas CODZP, NDZP, MDZP, MDBP, MDBO, MDZO, (Co-Mn)DZP, (Cd-Ni)DZP and (Cd-Co)DZHP crystals possessed *paramagnetism*.

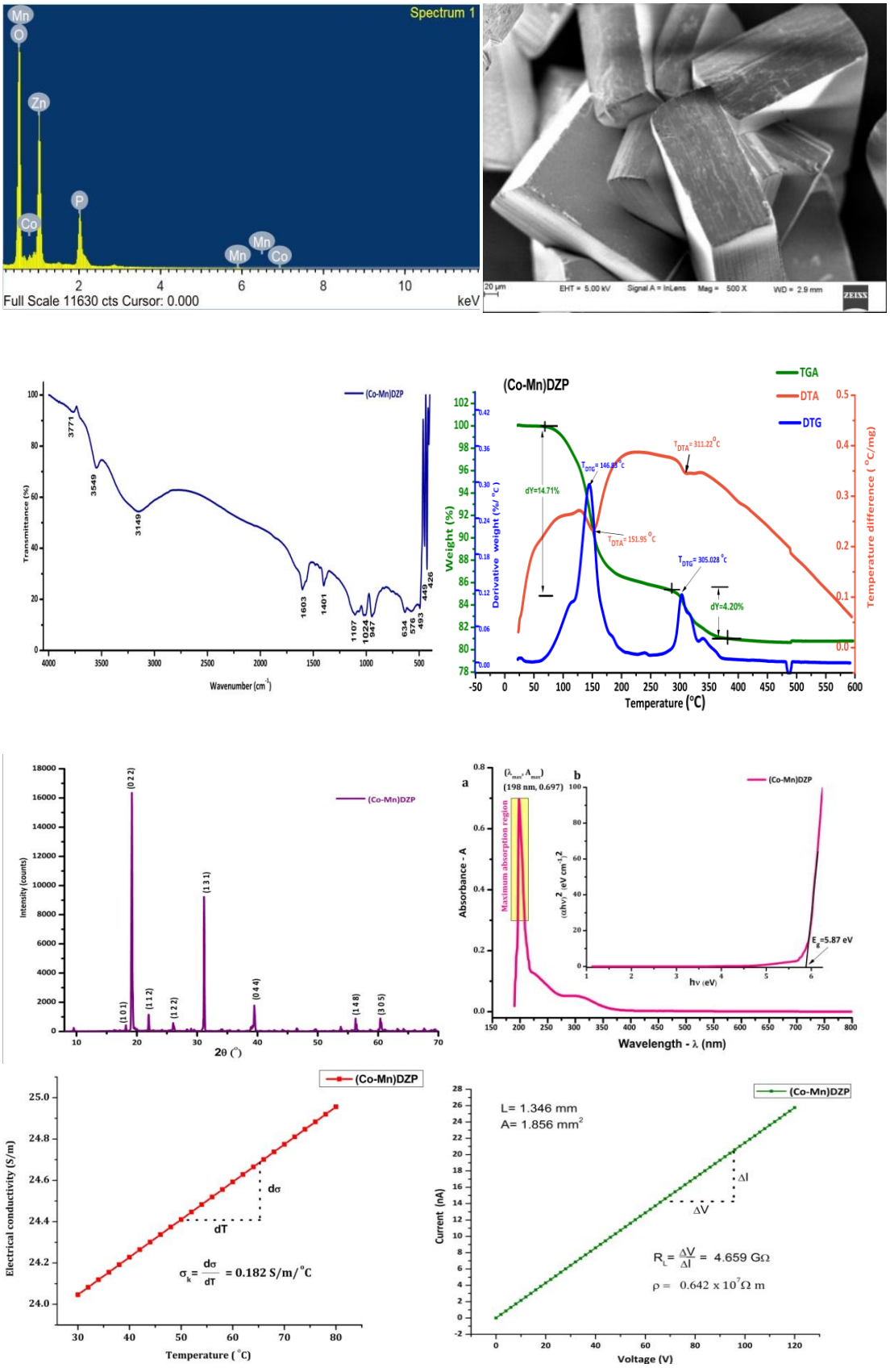

Figure 2. Characterization of doped phosphate and oxalate crystals.

Chapter 5: Impedance and resonance studies

Chapter 5 emphasizes on impedance spectrum and electrical resonance discharged by the crystal capacitors (fabricated using dielectrics of *MDBO, (Cd-Co)DZHP, CDZO, NDZP and (Co-Mn)DZP* crystals) which exhibited special electrical behavior. Response to alternating *emf* applied, the crystals vibrate and crystal capacitors show variation in reactance as a function of frequency. The mounting capacitance C_m varies from minimum 1.99pF ((Cd-Co)DZHP crystal) to maximum 10.33pF ((Co-Mn)DZP crystal). Crystals fabricated as capacitors exhibited series and parallel resonance in *mid-radio frequency* range (320 kHz to 5MHz). Resonance studies betrayed: two sharp resonance throws in frequency range 10kHz-20MHz, high *series quality factor* (Q_s range-729 to 2362), high *parallel quality factor* (Q_p range-6960.04 to 14000), ensured applications of MDBO, (Cd-Co)DZHP, CDZO, NDZP and (Co-Mn)DZP crystal capacitors in crystal oscillators, tuned amplifiers, radio receivers and rejecter circuits.

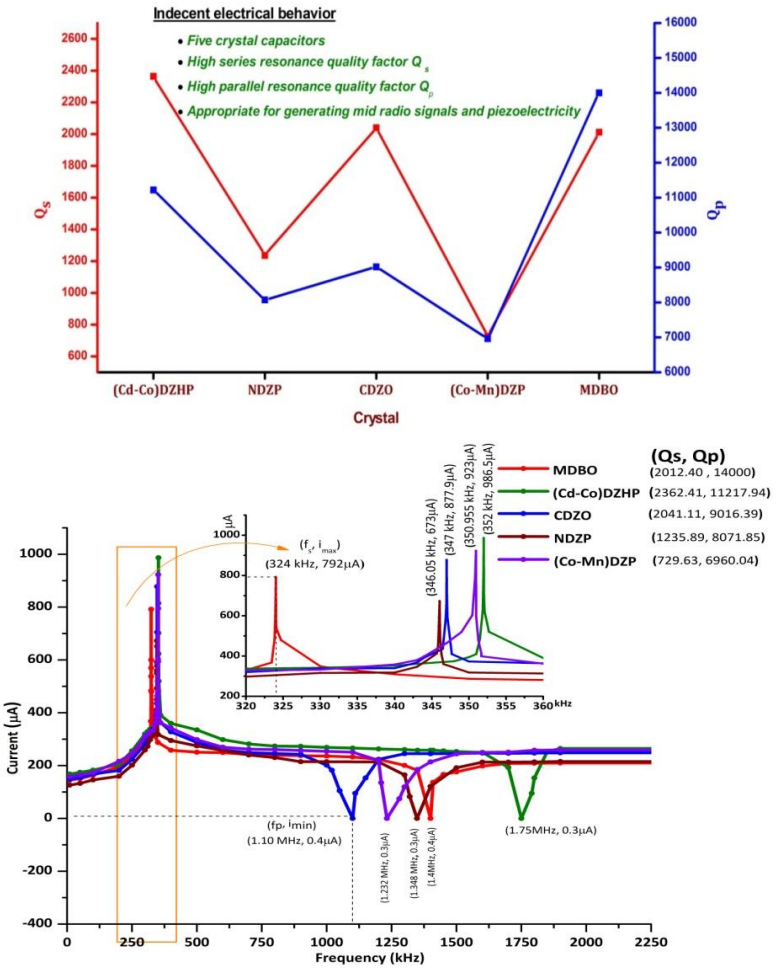

Figure 3. Resonance behavior.

Chapter 6: Summary

The concluding chapter 6 encapsulates the important observations, results and findings instigated during comprehensive study on growth and characterization of sixteen divalent doped phosphate and oxalate crystals. G_T diagrams were prospected to optimize PIS and OIS gels; which yielded three distinct series of high quality doped crystals. C_G diagram perusals demonstrated the growth dynamics of the crystals. This refined growth method opens multiple windows for further studies; which establishes the growth of enormous new crystalline materials in distinct gels and solvents.

Inherent physical and chemical properties were explored using spectroscopic and analytic techniques, which betrayed: cationic distribution, confirmed divalent doping and selective co-doping, crystal armature and geometry, decomposition behavior and thermal stability, molecular formula/weight, band gap energy, electric–magnetic-dielectric parameters ingrained in the crystals. Crystals inborn with nearly 6eV band gap energy, transparency in visible light, insulating behavior, thermal stability above 600^{o}C, very low current permittivity (nA), high dielectric constants, leakage resistance in GΩ, capacitance in pF and molar susceptibility χ; which ranges from 2.13×10^{-4} to 12.16×10^{-6}cm^3/mol. These results recommend spectrum of applications for the crystals in microelectronics and high temperature electronics.

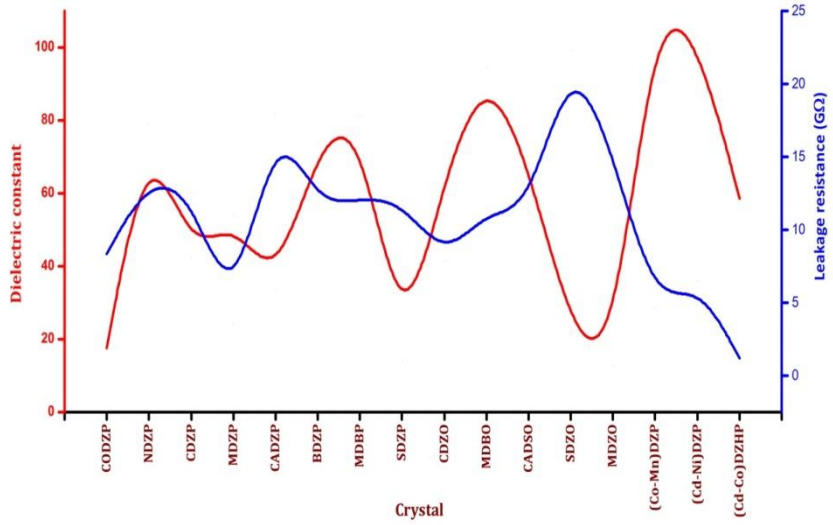

Figure 4. Variation of dielectric constant and leakage resistance with crystals.

Purity and clear surface fineness, water insolubility is the unique features of the grown doped crystals which provide very good corrosion resistance. As such, these crystals could be used as seed crystals in melt technique. Due to high dielectric

constants BDZP, MDBP, CADSO and (Cd-Ni)DZP crystallites be molded to use as *fillers* in PCB laminates. CODZP, MDZP, CADZP, SDZP, SDZO and MDZO crystals are most suitable to realize capacitance (pF to nF) and high *sheet resistance* (Ω/□) in monolithic integrated circuits. The chapter instigates more advanced studies for doped phosphate and oxalate crystals ingrained microelectronics. Doped crystals: MDBO, (Cd-Co)DZHP, CDZO, NDZP and (Co-Mn)DZP exhibited quartz like piezo-electricity, possessed high quality factors in turn could be used as *RF generators and rejecters*. However, more experimental studies are required to explore the applications of fabricated divalent doped, co-doped phosphate and oxalate crystals.

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List of publications

Publications related to the thesis

1. **Delma D'Souza**, Jagannatha, N., Nagaraja, K. P., and Reema, K. B. (2018). Effect of cadmium incorporation on optical and electrical properties of nickel doped zinc phosphate crystals. *Journal of Applicable Chemistry*, 7(3), 559-568.
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Growth Kinetics and Thermo-Opto-Electrical Properties of Cobalt Reinforced Zinc phosphate Crystals

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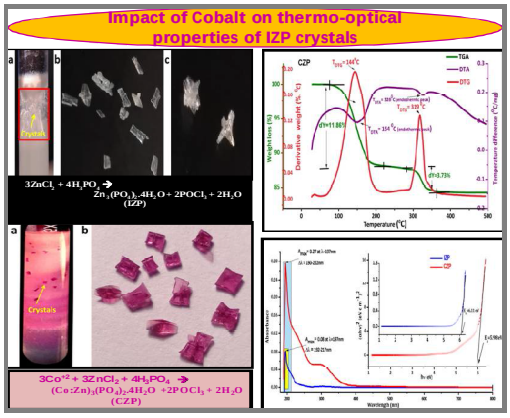
ABSTRACT

Cobalt doped zinc phosphate (CZP) and intrinsic zinc phosphate (IZP) crystals were grown by gel diffusion reaction technique. In the optimized growth environment with suitable Co^{2+} doping, pink coloured, hard, transparent CZP crystals were developed from the parent IZP crystals. Energy dispersive X-ray analysis (EDAX) identified Co^{2+}, Zn^{2+} and PO_4^{3-} ions complex in doped CZP crystals. FTIR spectral studies confirmed phosphate group, water molecule and M-O bond; which form armature of IZP and CZP crystals. Thermo gravimetric analysis (TGA) identified crystalline water, co-ordinated water and stability of the crystals in anhydrous phosphate phase above 500°C. P-XRD measurements depict high crystallinity of CZP and IZP crystals. IZP crystal propounded with a chemical formula $Zn_3(PO_4)_2(H_2O)_2.2H_2O$(molecular weight = 458.174) and CZP crystal manifested with a chemical formula of $(Co_{0.1228}\ Zn_{0.8772})_3(PO_4)_2H_2O.3H_2O$ (molecular weight=455.795) respectively. Optical studies unveiled insulating behaviour of parent and doped crystals. Co^{2+} cationic incorporation to Zn^{2+} vacancies increased the electrical conductivity. IZP and CZP possess dielectric constants of 18.32 and 17.53 in order. Investigation on growth aspects and thermo-opto-electrical properties merely highlighted the distinctness of CZP and IZP crystals.

Graphical Abstract



Keywords: Conductivity, Dielectric, Insulator, Silica gel, Thermal.

Thermal, Optical and Electrical Properties of Cadmium Doped Zinc Phosphate Crystals

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Abstract. Cadmium Doped Zinc Phosphate (CDZP) crystals were grown by gel technique using phosphoric acid impregnated silica gel. Good quality transparent CDZP crystals were born from the optimized growth environment. Chemical formula and molecular weight of test crystal was estimated by spectroscopic techniques. Energy Dispersive X-ray Analysis (EDAX) identified Cd, Zn, P and Oin doped ZP crystals. FTIR spectral studies confirmed phosphate group, water molecule and M-O bond. Thermo gravimetric studies unveiled stability of the crystals in anhydrous phosphate phase above 600^{o}C. The CDZP crystals conduct very small current in nA, possess leakage resistance in GΩ and capacitance in pF. Investigation on growth aspects and thermo-opto- electrical properties merely highlighted distinctness of novel CDZP crystal.

INTRODUCTION

In modern day scenario, particularly in the field of material science search for new and advanced materials is one of the prime concerns [1]. Certain new materials brought out show special properties to fitin active energy storage devices, ceramic glazes, auto extinguishing fibers, microelectronic and high temperature electronic applications.The special physical and chemical properties of materials can be better understood when it exist in the most ordered crystalline form [2]. Surprisingly, doping in intrinsic materials alters the morphology, physical, chemical and electrical properties. In fact, some of the doped crystalline materials exhibit good thermal stability, better dielectric strength and possess capacitance in pF [3]. In particular, phosphate crystals emphasizes NLO properties, luminescence and corrosion resistivity [4]. In a refined growth environment, adopting proper dopant, one can modify properties of the host crystal. In view of the above, our investigation was aimed at the growth of Cadmium Doped Zinc Phosphate (CDZP) crystals and studies onthermo-opto-electrical properties for special applications.

MATERIALS AND METHODS

Phosphoric acid impregnated silica hydro gel [5] was used to grow CDZP crystals. Chemicals used for growing CDZP crystals were Sodium Meta Silicate (SMS-$Na_2SiO_3.9H_2O$), Phosphoric acid (H_3PO_4), Zinc Chloride ($ZnCl_2$) and Cadmium Chloride ($CdCl_2.2.5H_2O$) of AR grade.

Silica hydro gel was prepared by mixing SMS solution with Ortho-Phosphoric Acid (OPA) in the ratio 5:4. To control premature gelling, OPA was added drop by drop to SMS with constant stirring and transferred to different test tubes for gelling. To the set gel the reactant mixture of 0.5M $ZnCl_2$ and 0.5M $CdCl_2$ were added along the sides of the test tubes. Zn^{2+} ions diffused through the porous polymerized gel and communicated with PO_4^{2-} ions. Cd^{2+} ions also diffused parallelly and occupied the vacancies of Zn^{2+} ions, which resulted in the formation of CDZP crystal. Growth conditions were optimized by varying gel parameters; specific gravities of SMS (1.03 - 1.07g/cm^3), concentrationsof OPA (0.5 - 2N), concentrations of reactant solution (0.25 - 2M) and ratios of Zn^{+2} to Cd^{+2}in reactant mixture (5 : 0.25 to 5: 2).Silica hydro gel of SMS specific gravity 1.0425g/cm^3 mixed with Phosphoric acid of concentration 1N in the ratio 5: 4optimized the gel and supernatant Zn^{+2} to Cd^{+2} ionsin the reactant mixture of 5:1 yielded good quality CDZP crystals. Chemical process involved in the formation of CDZP crystals is as follows.

$$3Cd^{+2} + 3ZnCl_2 + 4H_3PO_4 \rightarrow (Cd{:}Zn)_3(PO_4)_2.5H_2O + 2POCl_3 + H_2O.$$

Figure 1 illuminates the growth and extraction ofCDZP crystal.

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PAPER

Impact of Barium cationic mixing on Cadmium and Strontium oxalate crystals

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Keywords: mixed crystal, oxalate, electrical, dielectric

Abstract

Barium mixed Cadmium oxalate crystal (BMCO) and Barium mixed Strontium oxalate crystal (BMSO) were grown by single test tube gel technique using polymerized silica gel. Complexes of Cd^{+2}–Ba^{2+} ions and Sr^{+2}–Ba^{2+} ions in a controlled nucleation centres of gel media, stimulated the formation of BMCO and BMSO crystals. Resulted crystals are colourless, hard, transparent and exist in diamond like appearance. The grown mixed crystals were characterized using Energy dispersive x-ray spectroscopic (EDX) analysis, Fourier transform infrared (FT-IR) spectral studies, thermo-gravimetric (TG) studies and Powder x-ray diffraction (P-XRD). Investigation on BMCO crystal identified Cd^{+2}–Ba^{2+} ions cluster, matrix of coordinated water and crystalline water and good thermal stability with hexagonal crystalline nature. BMSO crystal associated with Sr^{+2}–Ba^{2+} ions complex, crystalline water, high thermal stability and crystallises in triclinic system. UV-visible spectroscopic studies determined band gap energies, transparency to visible light and insulating behaviour of the mixed crystals. Electrical conductivity measurements of the mixed crystals elucidated linear growth of conductivity with temperature. Both mixed oxalate crystals exhibit high dielectric constant values. Impact of Ba^{2+} ions diffusion into the lattices of BMCO and BMSO crystals were compared and discussed.

1. Introduction

In recent years production and applications of smart and new materials have attracted the attention of many investigators [1, 2]. Crystals like quartz possess high dielectric constant, exhibit piezo electricity, optically active, show double refraction and become smart material. Few researchers have concentrated their investigation on developing energy storage devices, ceramics and dielectrics, which have wide applications [2]. Over the years, particularly in Radio, Television, optical and Satellite communications modulation requires tolerance of the carrier frequency below 0.1% (crystal oscillators adopted quartz crystal possessed carrier wave tolerance nearly 0.1%). To attain above demands and to satisfy the needs of industries and laboratories, production of pure, high quality defect free crystals is essential. One of the most promising crystal growth methods to develop such crystals is gel technique. Gel method is a simple, inexpensive technique and supports the growth of alkaline, rare earth, transition metal complexes induced crystals [3–7]. Gel grown crystals are mostly water insoluble and bulk production is an added advantage.

Dharmaprakash *et al* reported the formation of Lissajous rings in Barium oxalate crystals [8]. Few investigators published their work on gel supported growth of doped tartrate and oxalate crystals [9, 10]. Recently, we have reported the matrix of Cr^{3+}–Cd^{2+} ions in oxalate crystals. Our present work mainly dealt on silica gel supported growth and characterization of Barium mixed oxalate crystals. Impact of Ba^{2+} ions induction on Barium mixed Cadmium oxalate (BMCO) and Barium mixed Strontium oxalate (BMSO) crystals were investigated. Interestingly, like quartz BMCO is hexagonal structured, whereas BMSO belongs to triclinic system.

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Effect of Cadmium Incorporation on Optical and Electrical Properties of Nickel doped Zinc Phosphate Crystals

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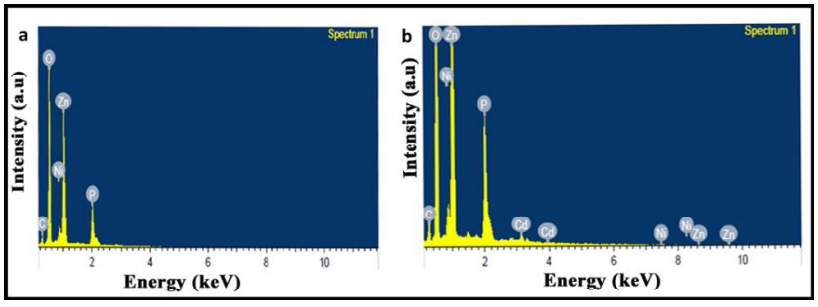
Accepted on 14th April 2018

ABSTRACT

Nickel doped Zinc Phosphate (NZP) and Cadmium incorporated NZP (CNZP) crystals were grown in silica hydro gel media. Specific gravity of Sodium Meta Silicate (SMS), gel setting time, pH of the gel, concentrations of ortho-phosphoric acid and concentration of supernatant solutions were varied to establish the optimum conditions for growth. Energy Dispersive X-ray (EDX) measurements predicted the matrix of Cd^{2+} ions with parental NZP crystal. FTIR spectral studies confirmed the presence of phosphate group, water molecules and metal oxygen link in NZP and CNZP crystals. Thermo Gravimetric Analysis (TGA) showed the thermal stability of the crystals upto 900^0C in their anhydrous state. From UV visible spectrophotometric studies band gap energy measured was 6.09eV for CNZP crystal. Electrical conductivity of NZP crystal is enhanced after incorporation of Cd^{2+} ion to form CNZP crystal.

Graphical Abstract



EDX spectrum of (a) NZP and (b) CNZP crystals

Keywords: Doping, Silica hydro gel, Nickel doped Zinc Phosphate (NZP), Cadmium incorporated NZP (CNZP).

INTRODUCTION

Crystals exist in most ordered form and are appropriate in understanding physical and chemical properties of solids [1]. Crystals like GaAs, CdS and InSb exhibit semiconducting behavior and they

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Growth, Characterization and Conductivity of Chromium Mixed Cadmium Oxalate Crystals

*Nagaraja Ponnappa, Jagannatha Nettar, Hema Mylnahalli, Delma D'Souza, and Lokanath Neratur**

Chromium mixed cadmium oxalate (CMCO) [Cr:Cd (C_2O_4).3H_2O] crystals are grown by gel diffusion method using silica hydro gel as growth media at ambient temperature. The optimum condition for growth is established by varying the parameters such as specific gravity, pH, gel aging, concentration of reactants and ratio of mixture Cd^{+2} to Cr^{+3}. Energy dispersive X-ray spectroscopy (EDX) confirms the existence of Cd^{+2} and Cr^{+3} ions in the crystal lattice of CMCO. Thermo-gravimetric analysis (TGA) reveal that, the CMCO are thermally stable up to 950 °C, which confirms the presence of three water molecules in the crystal lattice of CMCO. FT-IR spectrum exhibits the presence of OH, carboxyl group and metal-oxygen bonding. In this study, the occupation of vacancies of Cd^{+2} ions by Cr^{+3} cations in the lattice of mixed cadmium oxalate crystals without altering the morphology of the parent crystal is confirmed.

1. Introduction

Mixed crystals are of great importance in modern electronics; find their application in development of semiconductor lasers, diodes, crystal oscillators, etc. Crystals also exhibit special dielectric properties, which may be used in the production of metal oxide semiconductor field effect transistors and capacitors.[1] Certain mixed crystals show piezo-electricity, like quartz, which are used to filter radio frequency signals.[2] The development of lasers and masers has created new demand for mixed crystals in research and application. Oxalate crystals show special physical and chemical properties.[3] Barium doped oxalate crystals are pyrotechnical in nature which exhibit good thermal stability and hardness. Oxalate nanocrystals exhibit semiconducting properties, find their applications in high temperature electronics. Calcium oxalate crystals are used in ceramic glazes where as strontium oxalate crystals are used as auto-extinguishing fibers and in ammunitions.[4] Doping and changing the chemical composition of a crystal can generate new mixed crystals which will find many applications.[5,6] In the present investigation Cr^{+3} mixed cadmium oxalate crystals were grown by single test tube gel diffusion method using silica hydro gel as media of growth. The grown crystals were characterized and their optical properties and electrical conductivity were measured. The results obtained for chromium mixed cadmium oxalate (CMCO) crystals were compared with the intrinsic cadmium oxalate (ICO) crystals.

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2. Experimental

Mixed cadmium oxalate crystals were grown by single test tube gel diffusion method using silica hydro gel at room temperature. Sodium meta silicate solution (SMS) was prepared by dissolving 22 g of Na_2SiO_3 into 250 ml of distilled water with constant stirring and kept in dark and cool place. The SMS solution was diluted to attain specific gravity nearly 1.04. 0.5 M oxalic acid was prepared by dissolving 15.76 g in 250 ml of double distilled water.[7] SMS solution of specific gravity 1.04 was mixed with 0.5 M oxalic acid in a beaker by adding SMS solution drop by drop with constant stirring in the ratio 5:4. 9 ml of mixed solutions were collected in test tubes and allowed to set for four days. Once the gel set in the test tubes, the reactant mixtures of 0.5 M cadmium chloride and 0.5 M chromic chloride (ratio 5:1) were added. Diffusion of reactants into the gel results in the growth of CMCO.

The chemical reaction involved in the formation of mixed cadmium oxalate crystals is as follows.

$$CdCl_2.2.5H_2O + C_2H_2O_4.2H_2O \rightarrow Cd.(C_2O_4).3H_2O + 2HCl + 1.5H_2O$$

$$CdCl_2.2.5H_2O + Cr^{3+} + C_2H_2O_4.2H_2O \rightarrow Cr{:}Cd.(C_2O_4).3H_2O + 2HCl + 1.5H_2O$$

Our experimental results showed that the growth conditions of ICO and CMCO crystals are different. Specific gravity of SMS solution, aging of gel and its pH strongly influence the quality, purity, size and quantity of crystals.[8,9] In the present investigation, specific gravity of SMS solution resolved in between 1.02–1.03, 1.03–1.04, 1.04–1.05 and 1.05–1.06. Good quality and

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Magnesium and zinc diffused growth and characterization of strontium L(+) tartrate pentahydrate crystals

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Abstract:

Single crystals of intrinsic strontium L(+) tartrate (IST), Mg^{2+} doped strontium L(+) tartrate (MDST) and Zn^{2+} doped strontium L(+) tartrate (ZDST) are grown using gel diffusion method. Optimum condition for crystal growth is established by varying density of Sodium Meta Silicate (SMS) solution, gel pH, concentration and matrix of supernatant solutions. Stoichiometric composition and cationic distribution of the grown crystals are analyzed by EDAX measurements. Fourier transform infrared (FTIR) and Laser Raman spectral studies unveil various functional groups in the grown crystals. Thermo gravimetric analysis (TGA) confirms the presence of water molecules in the lattices and reveals decomposition behavior of the crystals in the temperature range of 30-1000 ^{o}C. Experimental data are used to generate the chemical formula for IST, MDST and ZDST crystals. IST crystals are found to possess a chemical formula: $SrC_4H_4O_6.5H_2O$ with a molecular weight of 325.77. MDST crystals show up with a chemical formula of $Sr_{0.9987}Mg_{0.0013}C_4H_4O_6.5H_2O$ (molecular weight 325.69) having a cationic distribution ratio: Sr^{2+}:Mg^{2+}=768:1. The ZDST crystal bears a chemical formula of $Sr_{0.9929}Zn_{0.0071}C_4H_4O_6.5H_2O$ (molecular weight 325.61) with a cationic distribution ratio: Sr^{2+}:Zn^{2+}=140:1. During the final stage of decomposition at high temperatures (761-1000 ^{o}C), the parent IST and the doped MDST and ZDST crystals attain stable state and exhibit thermal stability indicating usefulness of these crystals in high temperature electronics

Keywords: doped strontium tartrate, DSC, FTIR, gel technique, intrinsic strontium tartrate, Raman, TGA

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Growth and characterization of divalent transition metal ions doped zinc hydrogen phosphate single crystals

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Growth and Characterization of Divalent Transition Metal Ions Doped Zinc Hydrogen Phosphate Single Crystals

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Abstract. Zinc hydrogen phosphate (ZnHP) single crystal co-doped with divalent transition metal ions Cobalt (Co^{2+}) and Cadmium (Cd^{2+}) is grown by gel technique in silica hydro gel media. The presence of Co^{2+} and Cd^{2+} dopants in the ZnHP crystal was confirmed by Energy Dispersive X-ray Analysis (EDAX).FTIR spectra of the grown crystal depict the stretching and bending vibration of PO_4 units, water of crystallization and metal-oxygen bonds. Powder XRD analysis reveals that the grown crystal belongs to monoclinic system with spacegroup P 21. The thermal stability of the grown crystal is rectified from TG-DSC studies.

INTRODUCTION

Crystal growth in gels at ambient temperature is one of the simple inexpensive technique to get good quality crystals. Gel technique is suitable to grow crystals which are water insoluble and decompose before melting [1]. The physical and chemical properties of the parent crystal can be modified by introducing dopants at the time of growth. Many researchers have been reported the growth of phosphate crystals in gel [2-4]. On reviewing the past crystal growth studies it is found that very little investigations were done on transition metal ions doped phosphate crystals. Inorganic phosphate crystals show special physical and chemical properties that enable them to behave as catalyst, solid electrolyte for batteries, linear and nonlinear optical component, nutritional supplement etc., In the present investigation, Zinc hydrogen phosphate single crystal co-doped with divalent transition metal ions (Co^{2+} and Cd^{2+}) is grown by gel technique using silica hydro gel as media of growth. The grown crystal was characterized using Energy Dispersive X-ray analysis, FTIR analysis, Powder XRD and TG-DSC studies.

EXPERIMENTAL

Divalent transition metal ions Cobalt (Co^{2+}) and Cadmium (Cd^{2+}) doped zinc hydrogen phosphate (CoCdZnHP) single crystal is grown by single test tube gel diffusion technique using silica hydro gel at room temperature. The silica hydro gel was prepared by dissolving 22g Sodium Meta Silicate (SMS) into 250ml of double distilled water with constant stirring and kept undisturbed for five days and a clear stock solution was obtained on sedimentation [5]. Specific gravity bottle method is employed to determine specific gravity. SMS solution of specific gravity 1.04 to 1.07 g/cc was prepared. 1N orthophosphoric acid is added to SMS solution drop by drop with constant stirring in different ratios. Orthophosphoric acid behaves as the acidifying agent and also it provides the anions needed for crystallization of the compound. The mixed solution are collected in test tubes 9ml each and allowed to set for 1 day. Once the gel is set in the test tubes, the supernatant solution of 0.5M Zinc chloride and 0.5M Cobalt chloride and 0.5M Nickel chloride are added in the ratio 5 :1: 1 respectively. Diffusion of feed solution into the gel takes place which results in the growth of CoCdZnHP single crystal. The chemical reaction involved in the formation of single crystal is as follows.

$$Co^{2+}+Cd^{2+}+ZnCl_2.6H_20+H_3PO_4 \rightarrow Co:Cd:ZnHPO_4.H_2O+2HCl+5H_2O$$

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Growth, Characterization and Nucleation Reduction Mechanism of CCT Crystals in Silica Gel Medium at Different Environments

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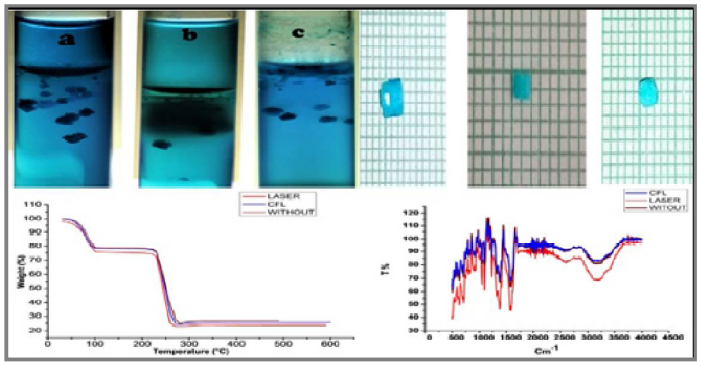
ABSTRACT

Cadmium doped Copper Tartrate (CCT) crystals were grown in silica gel medium using single diffusion methods at room temperature by passing semiconductor laser and other light radiations. Cadmium doped Copper Tartrate crystals were grown in three different growth faces to attain the total nucleation reduction. The metallic compositions in the crystals were estimated by Energy Dispersive X-ray Analysis (EDX). Thermo Gravimetric Analysis (TGA) of pure and Cadmium doped Copper Tartrate crystals suggest the possibility of the presence of co-ordinate water molecule in the crystalline structure. The functional groups present in the crystals were identified using Fourier transform infrared (FTIR) analysis. UV-Vis-NIR transmission spectrum was recorded to study the optical transparency of the grown crystals.

Graphical Abstract



Keywords: CCT, EDX, TGA, FTIR, UV-VIS-NIR.

INTRODUCTION

Single crystals are the backbone of the latest technology of logical innovation. In the present years crystals growth in gel medium has attracted the many investigators. Now a days great thinking has been devoted on the growth and characterization of doped crystals with the aim of determine new

Elemental Analysis and Thermal Studies of Cadmium Magnesium Oxalate Crystal Grown by Silica Gel Method

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Abstract: The Cadmium Magnesium Oxalate (CMO) crystals were grown by silica gel method. The optimum conditions were established by various parameters such as specific gravity of Sodium Meta Silicate (SMS), concentration of oxalic acid ($C_2H_2O_4$), pH of gel solution, gel setting time and reactant mixture ratio. Good quality CMO crystals were rectangular in shape with good morphology and transparent. Field Emission Scanning Electron Microscope (FESEM) image highlights the layer deposition growth of CMO crystal. Presence of Cd^{2+} and Mg^{2+} cations, O, C were confirmed by Energy Dispersive X-Ray Analysis (EDAX). TG studies revealed two steps of decomposition in the crystal due to dehydration and liberation of CO and CO_2 molecules. The chemical formula and molecular weight of CMO crystal were reported.

INTRODUCTION

Present day great attention has been devoted on growth and characterization of crystals. Crystals were backbone of the solid materials for modern technology. Applications of crystals noticed in the field of science and technology because of their interesting physical properties such as dielectric, ferroelectric, piezoelectric and non-linear optical properties [1]. Crystals grown in different methods among these, gel technique has been suitable. Crystals grown in gel technique are insoluble in water, inexpensive, and growing in ambient temperature [2].

MATERIALS AND METHODS

The Cadmium Magnesium Oxalate (CMO) crystals were grown in silica gel technique. The apparatus used for crystallization are simple glass test tubes of length 13cm and diameter 1.75cm. In a single diffusion gel method, gel was prepared by mixing Sodium Meta Silicate (SMS) of specific gravity 1.0403 g/cm^3 with solution of oxalic acid. The SMS was prepared by dissolving suitable amount of sodium meta silicate with distilled water. Solution of oxalic acid was prepared by dissolving 15.759 gm of oxalic acid with 250ml of distilled water. The mixture of SMS and oxalic acid solution was in the ratio 5:4 poured into the different test tubes. Gel was set in the different test tubes within 3-4 days. The reagents of cadmium chloride solution and magnesium chloride solutions were mixed in the beaker and poured drop by drop along the walls of the gel contained test tubes. The solution of cadmium chloride and magnesium chloride has molar concentration 0.5M. The growth of crystals completed within 15 days. Grown crystals were transparent and well shaped. Grown crystals are shown in FIG.1

FIGURE.1 a) Growth of CMO Crystals b) Extracted crystals

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